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Original Research Paper

Comparative study of seeding methods; dip-coating, rubbing and EPD, in SAPO-34 thin film fabrication

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ABSTRACT

Seeding methods; including rubbing, dip-coating and electro-phoretic deposition (EPD) were comparatively implemented for silicoalumino phosphate-34 (SAPO-34) thin film fabrication via secondary growth. The size of surface particles and thicknesses of fabricated layers were characterized by Scanning Electron Microscopy. The so-called properties were analyzed and modified to achieve a fairly defect free surface coverage and thin layers with finest particles. One-step dip-coating method provided well-distributed seeds on the support surface with a very poor coverage. Rubbing and EPD methods preferentially provided defect free and uniform surface coverage, however the grown particles from EPD method were bigger than those from rubbing method. It was revealed that in situ (no seeding) crystallization and one-step dip-coating method failed to produce defect free qualified membranes whereas EPD and rubbing methods caused continuous and defect free SAPO-34 membrane layers. To control synthesis parameters in the secondary growth crystallization, two important parameters were studied; crystallization time at three levels of 12, 24 and 48 h and crystallization temperature at three levels of 458, 473, and 488 K were simultaneously examined with the aforesaid seeding methods. Significant effects of crystallization temperature and time were observed on the formed layer qualities. The fabricated membrane by rubbing method during 24 h crystallization time at 473 K temperature was tested under equimolar gas mixture of hydrogen–methane at 293 K with pressure drops ranging from 1 to 6 bar. At one bar pressure drop, H_2 was enriched up to 84.2 mol% in the permeate side with the permeance of 6×10^{-8} mol/(m^2 s Pa).

1. Introduction

SAPO-34, a crystalline molecular sieve with chabasite structure has gained high attention for separating of light gases in membrane systems. High selectivity and permeability are the most important targets in preparation of qualified membranes which highly depend on synthesis method and conditions. Although in situ crystallization is an important and easy procedure for zeolite film growth on inorganic supports, recently secondary seeded growth is much more preferred due to the better control of size and orientation of crystals [1–3].

An effective seeding method is a mandatory step to have thin and defect-free zeolite membranes via hydrothermal synthesis of zeolitic layer on α-alumina and steel supports. The permeation properties of as-prepared membranes strongly depend on how the zeolite crystals are attached to the support in the seeding step during which the whole support surface should be covered uniformly and sufficiently [4]. Attaching seeds to the substrate can be achieved by means of; rubbing the zeolite crystals to the support surface [5–7], dip coating the support in a colloidal suspension of particles [8,9], electrophoretic deposition (EPD) [10–13], vacuum seeding [14], cationic polymer treatment [15], spin coating [16], etc. The simplest and often used method is to apply pre-synthesized crystals to the substrate by mechanical rubbing, which is not an ideal one since it is quite difficult to obtain a continuous and uniform seed layer [17]. Dip coating the substrate in a colloidal suspension of sub-micron-size zeolite particles followed by drying and sometimes calcination in order to fix the crystals to the support surface, is often repeated several times to ensure a sufficiently high coverage [18]. Electrophoretic deposition (EPD) is a simple, while effective technique for coating of charged particles on substrates [13] which offers several advantages including the uniformity of deposition, thickness control of the deposit, and reduction of waste often encountered in other coating methods [11].

In literature, there is rare information about comparative study of seeding methods for preparing SAPO-34 membranes and their

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effects on the membrane performance. In this work, three different seeding methods including rubbing, dip-coating and EPD are performed on tubular α-alumina supports followed by one time hydrothermal crystallization. Afterwards the surface layers are compared with in situ crystallization method. Effects of crystallization time and temperature are simultaneously investigated on the fabricated membranes by a factorial design, considering the mean sizes of surface particles, size distribution and layer thickness as the responses. Finally As a case study, one of the best membranes was examined for separation of H_2 and CH_4.

It should be noted that only limited studies have been carried out on H_2/CH_4 separation by SAPO-34 membrane. Poshusta et al. [19] reported H_2/CH_4 selectivity of 8.4 for an equimolar feed at 300 K using a SAPO-34 membrane. Hong [18] synthesized SAPO-34 membrane on tubular stainless steel (SS) support by in situ crystallization up to four layers to separate H_2 from CH_4, which showed selectivity of 28 and H_2 permeation around 2×10^{-8} (mol m^{-2} pa^{-1} s^{-1}) for a feed of 54/46 molar ratio at 293 K.

2. Material and methods

2.1. Synthesis of the seeds

The synthesis gel with molar ratio of Al_2O_3:P_2O_5:0.5SiO_2:2.2-TEAOH:100H_2O was prepared for synthesizing of SAPO-34 seeds. Aluminum isopropoxide (white powder, 98 wt%, MERK), colloidal silica in water (40 wt%, MERK), phosphoric acid (85 wt%, MERK) and tetraethyl ammonium hydroxide (TEAOH, 35 wt%, Aldrich) were used as the chemical sources. Aluminum isopropoxide was slowly added to stirring solution of H_3PO_4 and water to form a cream-like homogenous gel. Homogenizing the raw materials was carried out by a shaft mixer with 4500 rpm for 4–8 h. After 12 h of stirring, TEAOH was added before addition of colloidal silica. The resulting solution was sealed and aged at room temperature under magnetic stirring for 48 h. The prepared synthesis gels were poured in Teflon lined steel autoclaves which were thoroughly sealed to assure the autogenous pressure rise with temperature during the process. The crystallization step was performed at 458 K for 48 h, during which the gel mixture was magnetically stirred. After the hydrothermal synthesis the samples were cooled to room temperature, taking care not to impose thermal shock on the product. The samples were then washed with distilled water, centrifuged three times and dried at 373 K for 3 h.

2.2. Seeding method

The prepared seeds by the aforesaid procedure were applied on the surface of tubular α-alumina supports via Three methods of seeding; rubbing, dip-coating and EPD. In all methods, the porous tubular supports were cut into specific-size pieces and then boiled in distilled water for 30 min and cleaned in an ultrasonic bath to remove dusts and impurities, thereafter they were dried at 373 K for 3 h the Seeds were applied on the inner surface of α-alumina tubes in all designed experiments.

2.2.1. Rubbing method

α-alumina tubes were seeded by rubbing the inner side of the tubes with as-prepared SAPO-34 seeds using cotton swabs.

2.2.2. Dip-coating method

1.0 wt% aqueous suspensions of the seeds were prepared with the assistance of an ultrasonic bath to prevent formation of aggregates. Suspensions were then kept at room temperature for several days to let the heavy particles settle down. Alumina tubes were dipped in the suspensions for 45 min, and it was repeated with the tubes inverted for another 45 min to ensure the uniformity of seeding. Finally the seeded supports were dried at 373 K for 3 h.

2.2.3. EPD method

1.0 wt% aqueous suspension of the seeds were prepared according to Section 2.2.2. Firstly, α-alumina tube with its outside wrapped in Teflon tape was placed in a vessel filled with SAPO-34 seeds suspension, then a stainless steel rod was inserted vertically inside the support tube and was connected to the cathode of DC current, while The stainless steel vessel was used as the anode of the DC current. Fig. 1 shows a schematic view of EPD set-up. The distance between electrodes was set at 15 mm and deposition was carried out under a potential difference of 6 V between the electrodes for 1 h.

By applying a constant voltage, stainless steel rod became negatively charged and this charge was continuously transferred to the SAPO-34 seeds in the vicinity of the rod, consequently the charged particles migrated to the anode by means of electrical forces between the electrodes and finally deposited on the inner side of the tube which acted as an impermeable obstacle for SAPO-34 particles. Eventually, the tubes were dried at 373 K for 3 h.

2.3. Layer synthesis by secondary growth

The synthesis gel used for secondary growth had a molar composition of Al_2O_3:0.5SiO_2:1P_2O_5:1.5TEAOH:100H_2O and was prepared by the procedure described in Section 2.1. The seeded/unseeded supports were put in a Teflon-lined stainless steel autoclave with the synthesis gel in them; the crystallization process was carried out at different times and temperatures.

In order to analyze the effects of seeding method and crystallization time and temperature on the properties of formed SAPO-34 layer, three levels of crystallization temperature (458, 473 and 488 K) and three levels of crystallization time (12, 24 and 48 h) were design considering four levels of seeding: rubbing, dip coating, EPD and no seeding as described by 28 experimental runs in Table 1. The experiments were designed by the full factorial method, however the runs with simultaneous high crystallization times and high temperatures were omitted, since both time and temperature favor faster crystal growth and forming larger and undesired particles.

Characterization of the powder samples was carried out by XRD (X-ray diffraction) and SEM (scanning electron microscope) analyzers. The fabricated membranes were investigated by SEM analyzes to figure out the size of grown particles, size distribution and layer thickness. Table 1 summarizes the mean particle sizes and the film thicknesses which were calculated from SEM images.

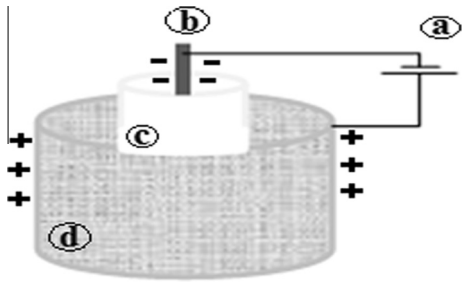

Fig. 1. Schematic of EPD set-up, (a) DC power supply, (b) stainless steel rod (cathode), (c) support and (d) stainless steel vessel (anode).